

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau


INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C11D 17/04, 3/39		A1	(11) International Publication Number: WO 95/16023
			(43) International Publication Date: 15 June 1995 (15.06.95)
(21) International Application Number: PCT/EP94/03924		(74) Agent: ELLIOTT, Peter, William; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).	
(22) International Filing Date: 25 November 1994 (25.11.94)			
(30) Priority Data:		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ).	
9325046.2 7 December 1993 (07.12.93) GB			
9406972.1 8 April 1994 (08.04.94) GB			
9413098.6 29 June 1994 (29.06.94) GB			
9415908.4 5 August 1994 (05.08.94) GB			
(71) Applicant (for AU BB CA GB IE KE LK MN MW NZ SD SZ TT only): UNILEVER PLC (GB/GB); Unilever House, Blackfriars, London EC4P 4BQ (GB).			
(71) Applicant (for all designated States except AU BB CA GB IE KE LK MN MW NZ SD SZ TT US): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).			
(72) Inventors; and		Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(75) Inventors/Applicants (for US only): SMITH, Gillian (GB/GB); 6 Daleside Close, Irby, Wirral, Merseyside L61 3XX (GB). SMITH, Royston, Reginald (GB/GB); 19 Brookhurst Close, Bromborough, Wirral, Merseyside L63 0LF (GB).			
(54) Title: TWO-PART CLEANING COMPOSITION COMPRISING AT LEAST ONE PEROXIDE COMPOUND			
(57) Abstract			
<p>Improved cleaning performance, especially as regards the removal of moulds, can be achieved by the use of two separate liquid compositions, a first of which contains an acid or neutral composition which comprises a peroxide and a second of which contains an alkaline composition, said first and second compositions being stored separately and sprayed from a single unit to a common point. By ensuring that these compositions are sprayed, either sequentially or simultaneously onto a surface where they react together to produce an alkaline peroxide solution, it is possible to overcome the problems of instability on storage and ensure that the mixed compositions are delivered at a pH at which the peroxide compound is active as a bleaching agent.</p>			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

WO 95/16023

PCT/EP94/03924

- 1 -

TWO PART CLEANING COMPOSITION
COMPRISING AT LEAST ONE PEROXIDE COMPOUND

5

FIELD OF THE INVENTION

The present invention relates to cleaning compositions which comprise at least two components which are stored separately and mixed shortly before use, at least one of said components comprising a peroxide compound. By peroxide compound is meant a compound comprising a peroxy (HOO-) group, including hydrogen peroxide and both organic and inorganic peroxides.

15

BACKGROUND TO THE INVENTION

The present invention provides compositions which are particularly well adapted for use in cleaning and sterilising household surfaces and the removal of discolouration caused by mould growth. Such discolouration is a known problem, particularly under humid conditions.

25

Compositions which remove, kill or bleach mould on surfaces have previously comprised strong solutions of alkali metal hypochlorite to be sprayed onto the surface. One problem with said compositions is that the hypochlorite has an unpleasant odour and, when sprayed, hypochlorite solutions can produce droplets which cause significant respiratory irritation.

Other bleaching agents are known, particularly peroxides. However, peroxides are often either unstable in

35

WO 95/16023

PCT/EP94/03924

- 2 -

formulations or exhibit poor bleaching performance at their most stable pH.

5 Toothpastes and peroxide-based hair bleaching compositions have been formulated as weakly acidic peroxide solutions or gels and separate weakly alkaline solutions or pastes which are mixed just before use. The known advantage of this form of product being that the peroxide is more stable to decomposition under acidic conditions and yet is
10 more effective as a bleaching agent under alkaline conditions.

Other two-part peroxide based compositions are disclosed in JP-A-60/038497 (LION BRANDS), which relates to a
15 foaming, two-part drain cleaning composition which comprises:

- a) 0.5-50%wt hydrogen peroxide,
- 20 b) alkali, having an alkalinity 0.1-50% based on sodium hydroxide,
- c) surface active agent in (a) or (b), and,
- 25 d) terpene alcohol/cyclic terpene alcohol in (a) or (b).

The compositions (a) and (b), including the surfactants and terpene are sequentially or simultaneously dosed into a toilet bowl and pass into the drains where the
30 composition produces a body of foam which acts to clean or if necessary unblock the drain.

Other forms of simultaneous delivery of two components are known.

35

WO 95/16023

PCT/EP94/03924

- 3 -

US 3760986 (CASTNER et al: 1973), discloses a dispensing bottle for dispensing two separate fluids to a common point. Such a bottle is formed with an opening at the top and a divider extending through the interior of the bottle to define two compartments which provide dual reservoirs for fluids. The apparatus disclosed further comprises pump means to simultaneously withdraw fluid from each compartment, via separate draw tubes, and discharge the fluid to a common point. This device enables an alkaline and an acid material to be stored separately and sprayed from a single unit to a common point. The pumps used in this apparatus are of a type wherein an inlet valve of a working chamber comprises a ball held against a valve seat by a spring such that as a piston compresses the working fluid the ball is forced against the seat and the working fluid cannot return down the draw tubes into the reservoirs.

The device disclosed in CASTNER is an integral package and dispenser. Although it can be envisaged that the device could be disassembled and refilled, such an activity could prove hazardous due to the nature of the liquids involved. CASTNER proposes that the device be provided with closable ports for refilling, although such an activity is envisaged to be dangerous where oxidising or corrosive liquids are concerned.

Some attention has been given to the provision of replaceable and/or refillable bottles in the general type of dual reservoir packaging mentioned above: e.g. EP 427609 (S.T.E.P.: 1991) and in WO/90/01959 (CORUS MEDICAL CORP: 1990) disclose spray means for attachment to a pair of bottles. In the first of these separate pumps are provided in each of the bottles. In the latter, the pumps are provided within the spraying heads and the bottles are

WO 95/16023

PCT/EP94/03924

- 4 -

connected to the spraying head by being impaled on needles which act as draw tubes.

5 US 4826048 (Pfeiffer: 1989) discloses a dispenser for pharmaceutical or cosmetic liquids which comprises a pair of bottles each provided with a separate pump. In this case, the bottles may be removed for refilling or replacement. US 5152461 (Proctor: 1992) discloses a
10 dispenser with a single pump and a pair of bottles which can be detached for refilling or replacement.

BRIEF DESCRIPTION OF THE INVENTION

15 We have now determined that improved cleaning performance, especially as regards the removal of moulds, can be achieved by the use of two separate liquid compositions, a first of which contains an acid or neutral composition which comprises a peroxide and a second of which contains
20 an alkaline composition, said first and second compositions being stored separately and sprayed from a single unit to a common point.

25 By ensuring that these compositions are sprayed, either sequentially or simultaneously onto a surface, whereby they react together to produce an alkaline peroxide composition, it is possible to overcome the problems of instability on storage and ensure that the mixed
30 compositions are delivered at a pH at which the peroxide compound is active as a bleaching agent.

DETAILED DESCRIPTION OF THE INVENTION

35 As described above, the invention provides a kit of parts comprising:

WO 95/16023

PCT/EP94/03924

- 5 -

a) a liquid, acidic or neutral composition comprising a peroxide compound stable at the pH of the acidic or neutral composition, and,

5 b) a liquid, alkaline composition,

said compositions being contained in separate reservoirs of a single unit adapted to produce a spray of at least one of (a) and (b).

10

By 'spray' the present specification means a spray of discrete droplets or a jet of foam, the operative consideration being that one or preferably both of the compositions are ejected from the unit with sufficient force that can be deposited upon a surface which is displaced horizontally from the unit.

15

It is preferred that the unit is adapted to produce a spray comprising a mixture of compositions (a) and (b).

20

In the alternative a unit can be adapted to produce separate sprays of compositions (a) and (b) such as by means of sequential spraying through a single spray means or simultaneous spraying through separate spray means. The production of a single spray which comprises a mixture of (a) and (b) is preferred.

25

A second aspect of the present invention provides a method of cleaning hard surfaces which comprises the steps of:

30

a) mixing a first, liquid, acidic or neutral composition comprising a peroxide compound with a second, liquid, alkaline composition so as to form an alkaline peroxide composition,

35

b) spraying the product of step (a) onto a surface to be cleaned.

WO 95/16023

PCT/EP94/03924

- 6 -

It is particularly preferred that the cleaning operation comprises the step of contacting the product of step (a) with the surface to be cleaned for a period in excess of 5 minutes.

5

Peroxides

The preferred peroxide compound is hydrogen peroxide although it is envisaged that other peroxides could be employed, provided that they are stable in the compositions of the invention.

10

As mentioned above, hydrogen peroxide shows better bleaching performance at an alkaline pH, particularly above pH 10. However, hydrogen peroxide shows reduced stability at this pH as compared with its stability at acid or neutral pH.

15

In the alternative, it is envisaged that other peroxide compounds can be employed. Among the preferred alternatives are peracids, particularly peracetic acid and persulphates particularly potassium mono-persulphate. While suspensions of solid peroxides can be employed it is preferred that solutions of a soluble peroxide are employed.

20

25

Such solutions are preferably aqueous although other solvents can be employed when the practice is chemically reactive with, or in the presence of water. Thus, in the presence of peracetic acid the diacetyl ester of ethylene glycol is a suitable solvent.

30

Preferred levels of peroxide compound range from 1-50%wt of the composition containing the peroxide compound. For hydrogen peroxide, levels below 4%wt peroxide are less

35

WO 95/16023

PCT/EP94/03924

- 7 -

effective as bleaching agents, whereas solutions containing more than 50%wt peroxide can be hazardous. For peracetic and persulphates levels of 1-10%wt in the neat compositions are preferred.

5

Mixing Ratio

As will be understood from the above an important aspect of the present invention is that two components are mixed either before or during the mixing operation. It is preferred that the mixing ratio falls into the range 2:1-1:2, with ratios around 50:50 being particularly preferred. It will be appreciated that the optimal mixing ratio will be to some degree dependent on the nature and quantities of the components present, the operative consideration being that the mixed composition should have an alkaline pH overall.

15
20

pH modifying agents

In order to attain the correct pH in the compositions which embody the present invention it can be necessary to add pH modifying agents.

25

In the case of acid solutions containing peroxides, further acidification may not be necessary. As is illustrated by the examples given hereafter, aqueous solutions according to the present invention can attain a natural acid pH. It is particularly preferred that the pH of the acid or neutral peroxide composition falls into the range of above 2 to less than 8, with preferred pH's being around 5. While solutions of pH below 2 can be used it is preferable to avoid such acid compositions due to hazards of spillage or contact with the skin of a user.

30
35

WO 95/16023

PCT/EP94/03924

- 8 -

In the case of alkaline compositions a pH above 10 is preferred. The most preferred pH range is 11-13. The alkaline reserve of the alkaline composition should be such that the pH remains high, preferably at pH 8 or above and more preferably above pH 10, after the addition of the acidic or neutral peroxide compound containing composition. However, the alkaline composition should preferably not have a pH so high as to be hazardous to use.

Where further acidification is required mineral or organic acids, with optional buffer salts, can be employed provided that these acids and salts are not peroxide sensitive. We have determined that di-sodium hydrogen citrate and/or trisodium citrate can be used to achieve the required acid pH. The presence of the trisodium citrate or other buffer salt being advantageous in that it prevent a downward drift in the pH of the acidic peroxide compound containing composition over prolonged storage.

Alkaline pH can be attained by the use of alkali earth or metal or ammonium hydroxides, particularly potassium and sodium hydroxides. Carbonates and/or bicarbonates can be present in the alkaline composition, as can borates, silicates, phosphates, and/or other buffers. Preferably the alkaline composition comprises 0.5-1.5 molar commercial caustic soda in aqueous solution.

In the method aspects of the present invention the alkaline and the acidic or neutral compositions can be mixed in any ratio between 1:10 and 10:1. The required ratio being somewhat dependent on the pH of the two compositions and the particular pH modifying agents present. As mentioned above, compositions should generally be formulated such that when mixed in a ratio of from 2:1-1:2, preferably, 1:1 the resulting solution has

WO 95/16023

PCT/EP94/03924

- 9 -

the desired pH, i.e. a pH at which the peroxide compound present is effective as a bleaching agent. For hydrogen peroxide the preferred pH after mixing with alkali is pH 10-12, more preferably pH 11-11.5. For monopersulphate and peracetic acid the preferred pH after mixing is around pH 8.

Thickeners

Thickener is an optional component of the present invention, being essential only in certain aspects of the invention. It is believed that thickeners can function in two ways.

We have determined that the presence of small amounts of thickener in at least one of said first and second compositions modifies the spraying behaviour of the composition to prevent the formation of an irritant mist. An irritant mist comprises relatively large population of fine droplets, whereas in the presence of a thickening agent a relatively small population of fine droplets is produced.

We have determined that certain cellulose derivatives, particularly hydroxy alkyl cellulose derivatives including hydroxy propyl methyl cellulose are particularly effective at thickening the acid peroxide composition to the extent required to achieve good spraying characteristics.

Second, thickeners can be selected such that the compositions thicken significantly when the components are mixed. This has the significant advantage that the composition does not run off sloping or vertical surfaces (such as the walls of shower stalls) when applied.

WO 95/16023

PCT/EP94/03924

- 10 -

Either or both of these characteristics of thickeners may be exploited in embodiments of the invention.

Typical levels of thickener range from 0.05-5%wt.

5

Typically, the thickener component is a polymer.

Where it is required that the compositions thicken on mixing, the most preferred thickeners are those which exhibit a marked increase in composition viscosity at above the pH of the acidic peroxide-containing composition.

10

Thus, in certain embodiments of the invention, the thickener is originally present in an acidic, peroxide compound containing composition at a pH where a low viscosity is exhibited, and, in use the solution is mixed with a more alkaline composition in a quantity such that the pH of the resulting mixture is one at which the thickener exhibits an increased viscosity.

15

20

Suitable polymers include those which only thicken compositions substantially at alkaline pH. Such polymers include polyacrylic acids (such as those available in the market as the 'Carbopol' (TM) series and acrylate copolymers.

25

We have found that a 2%wt solution of Acusol 820 (RTM ex. Rohm and Haas) an acrylate copolymer, forms a viscous gel at pH 6, whereas very little thickening is exhibited at pH 3.0. Lower levels of this polymer are employed when slight thickening so as to modify spraying behaviour are required. We have determined that acceptable spraying behaviour can be obtained when levels of this thickener of 0.05-0.5%wt are employed in the alkaline component.

30

35

WO 95/16023

PCT/EP94/03924

- 11 -

Alternative thickeners are those which exhibit poor thickening at very high pH. In embodiments of the invention where thickening on mixing is required, the thickener can be present in the alkaline composition, provided that the pH of this composition is sufficiently high, and that when an acidic or neutral peroxide-containing composition is added in sufficient quantity the pH falls into a region where an increased viscosity is exhibited.

Thickener components include clays, silicas, and mixed surfactant systems. Where significant thickening on mixing is required, the common factor between the thickeners is that when the acidic or neutral peroxide compound containing composition and the alkaline composition are mixed in the presence of the thickener components, the resulting mixture has a higher viscosity than either of the compositions taken alone.

From the above it can be seen that it is not essential for all embodiments of the invention that the thickener components are all peroxide stable, but only required that, where used, the or each thickener component is chemically stable in either the acidic or neutral peroxide compound containing composition or the alkaline composition.

Cationic Surfactant

It is preferred that at least one of said peroxide containing or alkaline compositions further comprises a cationic surfactant.

WO 95/16023

PCT/EP94/03924

- 12 -

Preferred cationic surfactants include the quaternary ammonium compounds of the formula:



5

Wherein R1-R4 are alkyl and X is an anion.

Preferably R1 and R2 are C8-C18 alkyl and R2 and R3 are C1-C4 alkyl. Preferably X is a halide.

10

Particularly preferred cationics include dialkyl dimethyl ammonium halides. We have determined that didecyl dimethyl ammonium chloride is particularly suitable.

15

We have determined that the abovementioned cationics are stable both in the alkaline solution and the acid peroxide solution and that no significant loss of peroxide occurs when the cationic is present in the peroxide compound containing composition, when the peroxide compound is hydrogen peroxide.

20

Other Surfactants

25

Other surfactants, in addition to the cationic surfactant, are generally present in the compositions of the present invention so as to assist in the cleaning process in which the compositions are used. The presence of further surfactant is however optional.

30

Whether the surfactants are required to be peroxide-stable or not will be determine whether the surfactant is incorporated in the acid/neutral or alkaline composition.

35

Preferred, peroxide-stable surfactants include anionic surfactants such as primary or secondary alkane

WO 95/16023

PCT/EP94/03924

- 13 -

sulphonates, primary alkyl sulphates and/or alkyl aryl
 sulphonates. Most preferable are nonionic surfactants,
 particularly those which comprise alkoxylated alcohols.
 Mixtures of two or more of these surfactants can be used.
 5 Alkyl sulphate surfactants and/or ethoxylated alcohols are
 particularly preferred.

Where the surfactants are unstable in acidic, peroxide
 containing compositions the surfactant can be provided as
 10 a component of the alkaline component. We have determined
 that ethoxylated alcohols are stable in either
 acid/neutral hydrogen peroxide solutions or alkaline
 solutions.

15 Typical levels of surfactants range from 0.1-20%wt of the
 component containing them. Levels of surfactant around 2-
 10%wt on total liquid component are particularly
 preferred.

20

Fungicides and Minors

Fungicides and/or other biocides, antimicrobials etc.
 other than the peroxides can be present, provided that
 25 they are stable in either the acidic/neutral component or
 the alkaline component.

Other minor components which are optional are perfumes,
 solvents, which may be required to solvate certain
 30 fungicides, and bleach stabilizers.

Bleach stabilisers will be required in the peroxide
 compound is decomposed by transition metals present in the
 composition. Accordingly it is preferable that the
 35 composition further comprises a transition metal
 complexing bleach stabiliser selected from phosphates,

WO 95/16023

PCT/EP94/03924

- 14 -

phosphonic acids or phosphonates, stannates, and carboxylates.

Preferred metal ion complexing agents are selected from
5 dipicolinic acid, ethylene diamine tetra acetic acid (EDTA) and its salts, hydroxy-ethylidene diphosphonic acid (Dequest 2010, RTM), ethylene diamine tetra (methylene phosphonic acid) (Dequest 2040, RTM), diethylene triamine
10 penta(methylene phosphonic acid) (Dequest 2060, RTM). The phosphonic acid derivatives are particularly preferred.

It is preferred that the level of metal ion complexing agent should fall into the range 0.01-5%wt, with levels
15 around 0.1%wt being particularly preferred.

While the reactions of peroxides with the transition metals have previously been though detrimental, the reaction can be used to advantage in the compositions of
20 the present invention. In an embodiment of the invention the alkaline component further comprises a transition metal or halide bleach decomposing agent which reacts with the acidic or neutral peroxide containing composition.

According to an embodiment of the invention in which the
25 acidic or neutral component comprises monopersulphate as the peroxy compound, the alkaline component comprises a halide, preferably a bromide. We have determined that when acidic monopersulphate solution and alkaline bromide solution are sprayed together onto a surface, so as to
30 give a final pH of around 8, a reaction occurs which produces hypobromite, an effective bleaching agent at pH 6 and above.

As mentioned above, solvents can be included in the
35 compositions of the invention so as to solvate components of the compositions. In addition, solvents can function

WO 95/16023

PCT/EP94/03924

- 15 -

to improve the cleaning and or wetting properties of the product as sprayed onto a surface to be cleaned.

Suitable solvents include the glycol ethers. A preferred solvent is BUTYL DIGOL (TM), which we have determined to be stable in the alkaline composition. Preferred solvent levels range from 2-12%wt with 3-8%wt being particularly preferred.

Apparatus

The apparatus aspect of the present invention provides for a two-part container which enables simultaneous or sequential spraying of compositions which comprise:

- a) a liquid, acidic or neutral, composition comprising a peroxide compound stable at the pH of the composition, and,
- b) a liquid, alkaline composition.

Such containers are known from the art and are described in US 3760986 (CASTNER et al: 1973), which discloses a dispensing bottle for dispensing two separate fluids to a common point.

It is particularly advantageous that the containers which define the reservoirs for the compositions comprise a draw tube, valve means to prevent liquid returning along said draw tube and means to releasably engage said container with a pumping and spraying head.

The container described above is of particular utility when used in combination with a dual-reservoir pumping and spraying head of the type described with reference to the

WO 95/16023

PCT/EP94/03924

- 16 -

background of the invention. Whereas the prior art envisages that the containers alone can be disassembled from the spraying apparatus, or that the containers be disassembled from the spraying apparatus together with an associated pump, there is no disclosure of a container with an integral draw tube and non-return valve which can be removed from the pumping and spraying apparatus.

In such an embodiment as is described above it is essential that the valve means allows liquid to be drawn from the container when the container is engaged with the pumping and spraying head. Suitable valve means include a valve seat and a check element urged against the seat by spring means. It is preferred to use a ball valve urged against an annular seat by a helical spring.

In preferred embodiments of the invention said valve means further comprise means to prevent discharge of the contents of the container prior to attachment of the spray head. This feature is particularly useful if the contents of the container are chemically aggressive, i.e. if corrosive or oxidising contents are employed.

Said means to prevent discharge can comprise a membrane closing the egress from the container. The arrangement being such that the membrane is pierced before or as the container is engaged with the pumping and spraying head.

Particularly preferred containers have a second valve means which acts to prevent discharge of the container contents when the container is not engaged with the pumping means. Such a construction has the advantage that a partially empty container can be disengaged from the pumping and spraying head without risk that the contents will be discharged. In one such embodiment a second check element is held against a second valve seat by spring

WO 95/16023

PCT/EP94/03924

- 17 -

means, unless displaced by a member projecting from the pumping and spraying head.

5 The invention extends to the containers described above filled with an aqueous solution of a peroxide compound and/or alkali. All of these species are either corrosive or otherwise harmful and gas-evolving reactions can occur when they are mixed.

10 A further advantage of containers according to the preferred embodiment of the present invention is that the valve means prevents the container being refilled by an unskilled or ill-informed user. If the containers could be refilled with ease, a user might be led to operate a
15 dual reservoir pumping and spraying device of the type described above with solutions such as hypochlorite and strong acid, which produce a potentially deadly cloud of chlorine gas when these solutions are allowed to react.

20 In order that the present invention can be further understood it will be described hereinafter by reference to non-limiting examples and with reference to the accompanying figures wherein:

25 FIG 1 and 1a: show a container according to the present invention, in isolation as in figure 1a or assembled together with a similar container and a spraying and pumping head.

30 FIG 2 and 2a show alternative embodiments of the invention with particular detail of the valve means.

FIG 3 shows a detail of a preferred valve means in an embodiment of the present invention.

35

WO 95/16023

PCT/EP94/03924

- 18 -

EXAMPLESEXAMPLE 1: compositions

5 Unglazed ceramic tiles (simulating glazed tile grout) were treated with a fungal liquid medium (Saboraud Liquid Medium) and inoculated with spores of *Penicillium chrysogenum* (a green mould common in bathrooms and kitchens) by exposure of the tiles to spores released from
10 a culture of the fungus maintained on an agar plate (Czapek Dox agar + 2% malt extract). The tiles were stored in damp conditions (relative humidity around 90%) to encourage growth and the backs of the tiles were sprayed with water to maintain conditions which favoured
15 growth of the mould. The tiles were used as such to evaluate the effect of the composition of the invention on fresh mould, whereas the effect of the composition on aged mould was determined after autoclaving of the tiles.

20 Two separate solutions, 'Composition A' and 'Composition B' were made up as follows, the components being added to distilled water to reach the given final concentration. Additions were in the order listed, with a five minute stirring period between each addition.

25

Composition A:

0.15%	Methocell J12MS (hydroxy propyl methyl cellulose),
0.2%	DEQUEST 2060 (TM ex. Monsanto),
30 6.0%	Hydrogen Peroxide,
1.0%	Disodium hydrogen citrate,
4.0%	NE-208T (TM ex. Nippon Oil) primary alcohol ethoxylate, nonionic surfactant,
0.2%	Perfume

35

WO 95/16023

PCT/EP94/03924

- 19 -

composition 'A' was adjusted to pH 5.0 with 20% sodium hydroxide solution.

2% Methocell solution was prepared by gradually adding the polymer to distilled water and stirring to disperse. The dispersion was heated to approximately 60 Celcius and the pH adjusted to 9.0 with NaOH. The solution was stirred for around one hour while cooling to ambient to give a clear viscous stock solution.

10

Composition B:

	0.1%	ACUSOL 810 (TM ex. Rohm and Haas): acrylic crosslinked copolymer,
	1.9%	NaOH
15	4.0%	NE-208T (TM ex. Nippon Oil) primary alcohol ethoxylate, nonionic surfactant,
	1.0%	Didecyl dimethyl ammonium chloride,
	4.0%	BUTYL DIGOL (TM),

20 These compositions were separately loaded into identical trigger spray bottles and sprayed simultaneously from a single unit onto the same region of a tile prepared as described above while the tile was maintained with a near vertical slope. A small amount of foam formed on the surface of the tile and remained. It was determined that aged (autoclaved) mould was partially bleached over a period of 20 min whereas substantial bleaching of fresh mould occurred in the same period. After overnight treatment (around 14 hours) nearly complete bleaching of both fresh and aged mould was observed.

30

It was determined that optimum bleaching was achieved with a 1:1 mixing ratio.

WO 95/16023

PCT/EP94/03924

- 20 -

Storage tests for up to 32 days showed that the was comparatively little loss of peroxide and/or cationic in the separately stored solutions.

5

EXAMPLE II: apparatus

Figures 1 and 1a shows container [1] with draw tube [2] and valve means [3] in the upper surface [4].

10

In figure 1 the container [1] is assembled together with a second container [11] and a spraying and pumping head [10]. When the spraying and pumping head is operated, liquid is drawn by pump means within the head from each of the containers [1] and [11], mixed, and ejected in the form of a spray via nozzle [12].

15

Figures 2 and 2a show detail of the valve means [3] in the upper surface [4] with the pumping and spraying head [10] removed. The valve means [3] comprise a cylindrical body with openings at opposed ends. The body houses a spring means such as helical spring [7] and a check element such as ball [6]. Unless disturbed, the spring means [7] urges the check element [6] against a valve seat [7a] to prevent flow of liquid from within the cylindrical body into the draw tube [2]. When assembled as in figure 1 the pumping means within the pumping and spraying head [10] are connected to the valve means [3]. Latching means, such as fittings [5] are provided to assist and maintain engagement of the valve means [3] with the spraying and pumping head [10].

20

25

30

In the embodiments shown in figures 2 and 2a means are provided to prevent egress of liquid from within container [1] before the container [1] is attached to the spraying and pumping head.

35

WO 95/16023

PCT/EP94/03924

- 21 -

In figure 2a said means comprise a membrane [9] which closes the upper opening of the cylindrical body until pierced by an element within the spraying and pumping head: in this embodiment the seat of the spring [7] is provided by stop [9a] upon which defines an aperture closed by the membrane. A particular advantage of this embodiment is that it is tamper-evident.

In figure 2 said means comprise a second ball valve which comprises a valve seat [8a] against which ball [8] is urged by spring 7. In the embodiment shown in figure 2 an element within the spraying and pumping head pushes the ball [8] off the seat [8a] when the valve means [3] are engaged with the spraying and pumping head. A particular advantage of this embodiment is that the second ball valve closes when the container [1] is detached from the spraying and pumping head [10].

Figure 3 shows further detail of the valve means [3] in the upper surface [4] with the pumping and spraying head [10] removed. As in figures 2 and 2a the valve means [3] comprise a cylindrical body with openings at opposed ends. The body again houses a spring means such as helical spring [7] and a check element such as ball [6]. Latching means, such as fittings [5] are provided to assist and maintain engagement of the container with the spraying and pumping head [10]. Figure 3 also shows a venting aperture [13] and a porous plug [14] located between the body and the outer shroud [15]. The venting aperture [13] allows gas generated within the container [1] to escape. The aperture [13] also allows air to flow into the container so as to equalise the pressure within the container with the ambient when the liquid contents of the container are removed by the spraying and pumping head via the draw tube [2].

WO 95/16023

PCT/EP94/03924

- 22 -

In use, pumping means within the spraying and pumping head [10] generates a partial vacuum in the cylindrical body: excess pressure within the container [1] forces liquid up the draw tube [2] and urges ball [6] off the seat [6a] against the resistance of the spring [7]. Liquid can then flow from the container [1] to into the spraying and pumping head. Within the spraying and pumping head [10] liquids from containers [1] and [11] are mixed prior to ejection through the nozzle [12]. When operation of the spraying and pumping head ceases, flow of the mixed liquids back into container [1] is prevented by ball [6].

15

WO 95/16023

PCT/EP94/03924

- 23 -

CLAIMS

1. A kit of parts comprising:

5

a) an liquid, acidic or neutral composition comprising a peroxide compound stable at the pH of the composition, and,

10

b) an liquid, alkaline composition,

said compositions being contained in separate reservoirs of a single unit adapted to produce a spray of at least one of (a) and (b).

15

2. Kit according to claim 1 wherein at least one of composition (a) or composition (b) further comprises a cationic surfactant.

20

3. Kit according to claim 2 wherein the cationic surfactant is a quaternary ammonium compounds of the formula:



25

wherein R1-R4 are alkyl and X is an anion.

4. Kit according to claim 3 wherein R1 and R2 are C8-C18 alkyl and R2 and R3 are C1-C4 alkyl.

30

5. Kit according to claim 1 wherein component (a) comprises hydrogen peroxide, a monopersulphate salt, peracetic acid or a mixture thereof.

WO 95/16023

PCT/EP94/03924

- 24 -

6. Kit according to claim 1 wherein at least one of components (a) and (b) further comprises a thickener component.
- 5 7. Kit according to claim 6 wherein component (a) comprises a thickening modified cellulose.
8. Kit according to claim 6 wherein component (a) comprises an acrylic crosslinked polymer.
- 10 9. Kit according to claim 1 wherein at least one of components (a) and (b) further comprises an ethoxylated alcohol anionic surfactant.
- 15 10. Kit according to claim 1 wherein at least component (a) further comprises a metal ion complexing agent.
11. Kit according to claim 1 wherein at least component (b) further comprises a glycol ether solvent.
- 20 12. A method of cleaning hard surfaces which comprises the steps of:
 - a) mixing a first, liquid, acidic or neutral
25 composition comprising a peroxide compound with a second, liquid, alkaline composition so as to form an alkaline peroxide composition,
 - b) spraying the product of step (a) onto a surface
30 to be cleaned.

Fig. 1 is a perspective view of a container 1. A vertical tube 2 extends from the bottom of the container. A cap 3 is fitted onto the top of the tube, and a seal 4 is positioned between the cap and the container's neck.

WO 95/16023

2 / 2

PCT/EP94/03924

Fig.2.

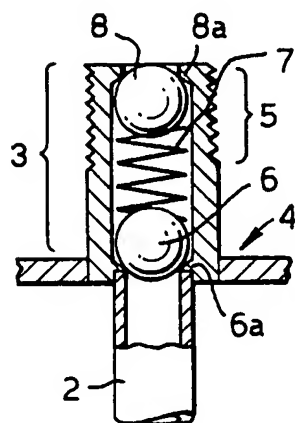


Fig.3.

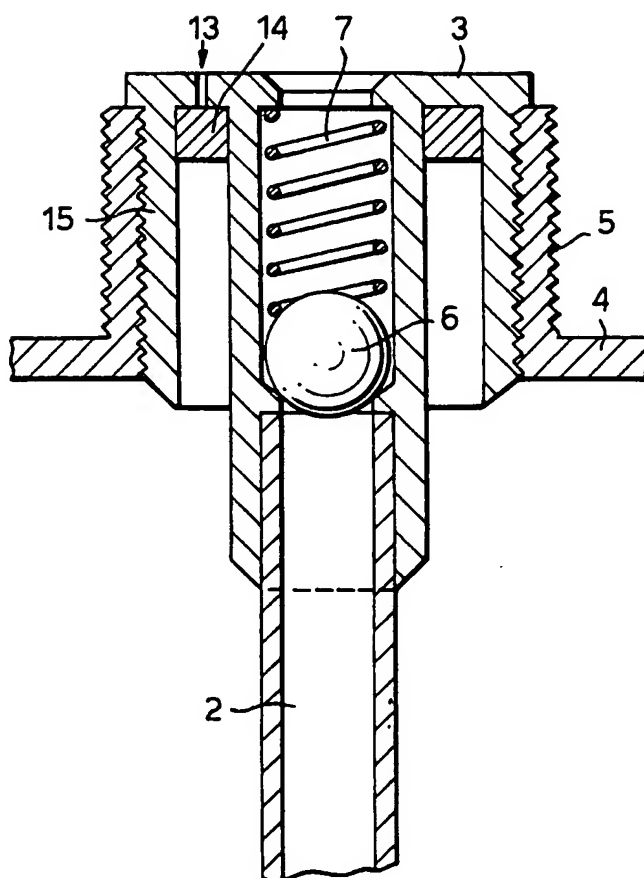
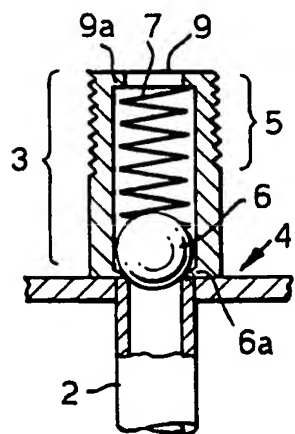


Fig.2A.



INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 94/03924

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D17/04 C11D3/39

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 8515 Derwent Publications Ltd., London, GB; AN 85-089699 & JP,A,60 038 497 (LION CORP.) , 28 February 1985 cited in the application see abstract	1,12
A	US,A,3 760 986 (CH. S. CASTNER ET AL.) 25 September 1973 cited in the application see the whole document --- -/--	1

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

10 May 1995

Date of mailing of the international search report

15.05.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Bellingen, I

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 94/03924

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p> DATABASE WPI Week 8214 Derwent Publications Ltd., London, GB; AN 82-27811E & JP,A,57 038 102 (MITSUBISHI GAS CHEM. IND.) , 2 March 1982 see abstract ----- </p>	<p> 1,2,5, 10,12 </p>

Information on patent family members

PCT/EP 94/03924

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3760986	25-09-73	NONE	